



Department of Pesticide Regulation



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MEMORANDUM

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SUBJECT: SURFACE WATER MONITORING FOR FORESTRY HERBICIDES
IN THE YUROK ABORIGINAL TERRITORY OF THE KLAMATH
RIVER WATERSHED, SPRING 2000

SCOPE OF THIS MEMORANDUM

The purpose of this memorandum is to provide results of water sampling conducted in the Klamath River watershed by the Department of Pesticide Regulation (DPR). This study was initiated, in conjunction with the U.S. Environmental Protection Agency and the Yurok Tribe, to address tribal concerns about the potential presence of herbicide residues in surface water. Tribal people live adjacent to land owned by a timber company that uses herbicides for forestry management. This memorandum summarizes the third sampling results of a three-year study, initiated in 1998, designed to monitor the occurrence of forestry herbicides, atrazine, triclopyr, glyphosate, and 2,4-D, in selected creeks of the Klamath River watershed. Data included here are from April 20 to May 15, 2000, with results from chemical analysis. An in-depth interpretation of the data is not included here but will be provided in the final report, which will include data from all three years of the study.

Sample and Data Collection

On April 23 and 24, 2000 surface water samples were collected from a tributary (site I) and creek (site J) flowing through the buffer zone of two aerial application sites (Table 1, Table 2, Figure 1). Samples were collected in the buffer zones immediately following application and through the application period. All samples were taken at eight time intervals for each site. In addition, herbicide samples were collected from the batch mixture in the spray tank to be applied at each site.

Runoff samples were collected during the first rainfall event following application to produce significant increase in water level at the sample sites. On April 16 and 25, 2000, samples were collected from a creek and tributary below atrazine ground application sites (site H and K) (Table 1, Table 3, Figure 1). On April 25 and 27, 2000 samples were collected from three



creeks (site J, L and M) below the aerial application sites (Table 1, Table 3, Figure 1).

Table 1. Forest site and herbicide application descriptions in Del Norte County.

Site (Unit #)	Description	Application type	Application date	Application time*	Acres treated	Total AI used (lb)	Application slope (%) ^a	Intermediate slope (%) ^b
H (215)	Bear Creek	Ground	3/23/00	N/A	36	143 lb. Atrazine 22 lb. Triclopyr	30	30
I (19)	West Fork Hunter Creek Tributary	Aerial	4/23/00	08:21	245	245 lb. Triclopyr 245 lb 2,4-D	34	30
J (15,16)	West fork Hunter Creek	Aerial	4/24/00	11:12	230	230 lb. Triclopyr 230 lb. 2,4-D	44 to 60	20 to 53
K (203)	Blue Creek Tributary	Ground	4/24/00	N/A	80	260 lb Atrazine	56	9
L (7)	West Fork Hunter Creek	Aerial	4/24/00	N/A	20	20 lb. Triclopyr 20 lb. 2,4-D	44 to 60	20 to 53
M (8)	Hunter Creek	Aerial	4/24/00	N/A	100	100 lb. Triclopyr 100 lb. 2,4-D	30	10

a=change in elevation from top to bottom of application site (ft)/distance (ft) X 100

b=change in elevation from bottom of application to sampling site (ft)/distance (ft) X 100

Elevation and distance estimated on USGS 7.5 minute Quad maps

*recorded only for an application sampling site.

Table 2. Descriptions of application sampling-site in Del Norte County.

Site	Description	Coordinates	Elevation*	Distance from application site
I	West Fork Hunter Creek Tributary	41° 38' 20.1" N 124° 00' 33.6" W	680 ft	200 ft
J	West Fork Hunter Creek	41° 37' 36.2" N 124° 01' 18.5" W	240 ft	400 ft

* = Elevation estimated on USGS 7.5 minute Quad maps

Table 3. Descriptions of runoff sampling-site in Del Norte County.

Site	Description	Coordinates	Elevation*	Distance from application site	Precipitation (inches) ^a
H	Bear Creek	41° 24' 13.6" N 123° 55' 25.2" W	80 ft	500 ft	1.22
J	West Fork Hunter Creek	41° 37' 36.2" N 124° 01' 18.5" W	240 ft	150 ft	0.55
K	Blue Creek Tributary	41° 27' 27.0" N 123° 54' 22.9" W	1160 ft	1300 ft	0.46
L	West Fork Hunter Creek	41° 31' 55.0" N 124° 00' 23.6" W	160 ft	200 ft	0.72
M	Hunter Creek	41° 35' 46.7" N 124° 01' 35.6" W	160 ft	1600 ft	0.63

* = Elevation estimated on USGS 7.5 minute Quad maps

a = Total precipitation from application date to sampling date, gauged at the sampling site.

All water samples were collected as a grab sample from the main flow of the creek, using an ISCO automatic sampler. All samples were stored on wet ice or in a 4°C refrigerator until analysis.

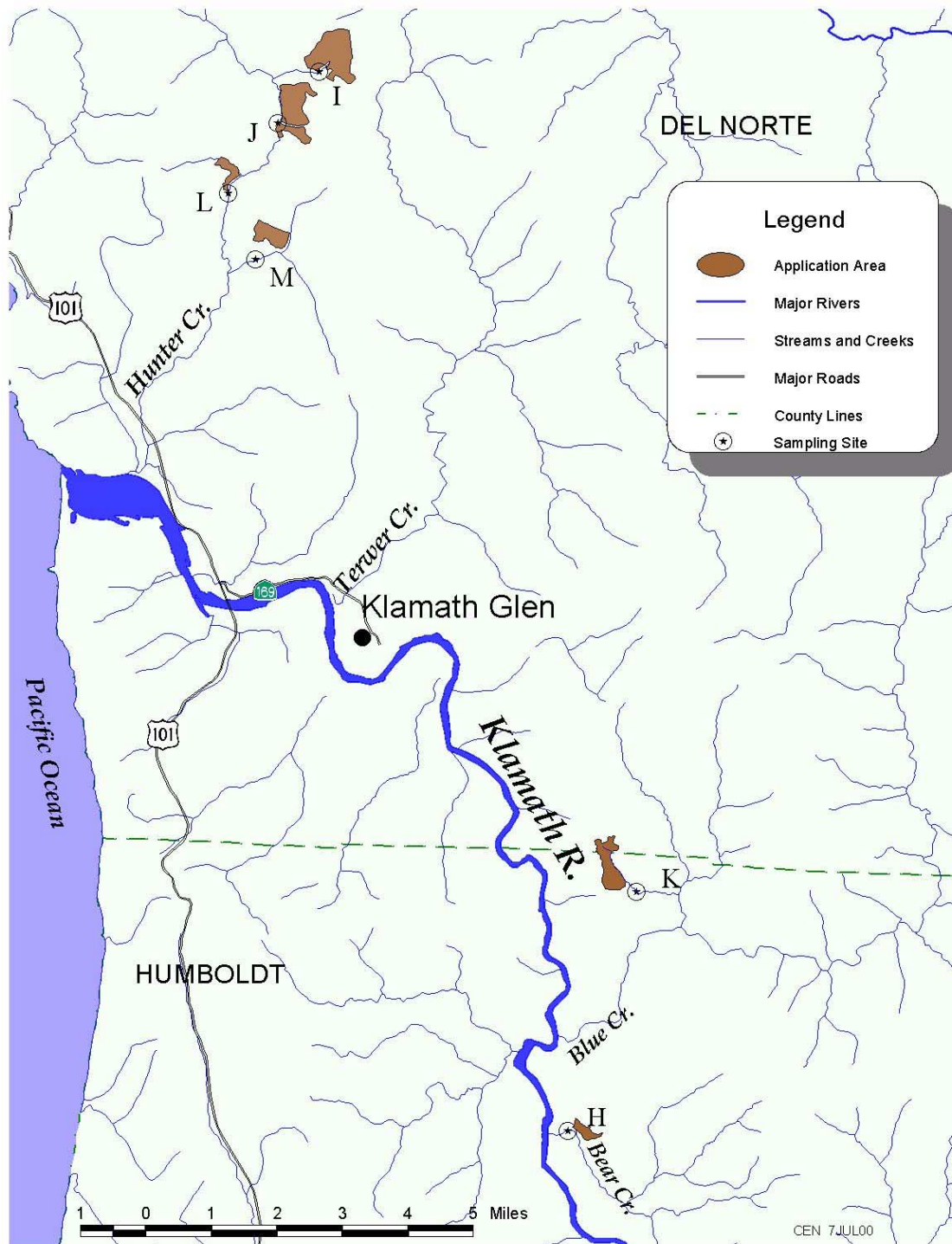


Figure 1. Application and sampling sites in Del Norte and Humboldt Counties

Environmental Measurements

Water quality parameters measured *in situ* included temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO). Water pH was measured using a Sentron (model 1001) pH meter. Water temperature and EC were measured using an Orion conductivity-salinity meter (model 140). DO was measured using an YSI dissolved oxygen meter (model 58).

Herbicide Analyses

Herbicide analyses of water samples were performed by the California Department of Food and Agriculture Center for Analytical Chemistry. Atrazine, a triazine herbicide, was analyzed using high performance liquid chromatography (HPLC) with an ultraviolet (UV) detector, and gas chromatography (GC) with a nitrogen phosphorus detector (NPD). The phenoxy herbicides, 2,4-D and triclopyr, were analyzed by GC on a capillary column using a mass selective detector (MSD). The reporting limit (reliable detection level) for atrazine is 0.05 parts per billion (ppb), and 0.10 ppb for 2,4-D and triclopyr.

RESULTS

Herbicide Concentrations

Table 4 presents the results of the four tank samples analyzed for the percentage of chemical mixed in each application batch. According to the label guidelines for forestry management application rates, the maximum allowable are atrazine-ground, 4%; triclopyr-ground, 4.4%; triclopyr-aerial, 2.2%; 2,4-D-aerial, 2.5%. All applications were made within the label rates except the first ground application which had a concentration of 4.47% atrazine. This may have been due to incomplete mixing of the tank mixture or settling of the chemical.

Application samples were collected at two separate application areas, Site I on a tributary in to the West Fork of Hunter Creek, and Site J located on the West Fork of Hunter Creek (Table 5). Samples were collected at the completion of the application to the buffer zone and for additional intervals during the application to the remaining treatment area. At Site I, 2,4-D and triclopyr were detected at a concentration range of 0.163 ppb to 0.584 and 0.223 ppb to 1.06 ppb, respectively, during the time of application to the treatment area. No detections were found in samples collected at Site J on April 16, 2000.

There was no detectable amount of atrazine in the storm runoff samples from either of the ground application areas (Table 6). One storm runoff sample was collected (site J) on April 25, 2000. 2,4-D was detected at 0.103 ppb and triclopyr was detected at 0.122 ppb. At the time, it appeared there was not enough precipitation for runoff to occur; therefore, no further

samples were collected from this site and the sampler was relocated further downstream. The new site (L) provided runoff from 4 application sites. Sample collection began approximately three days after the last unit in this area was applied. Samples collected during a rain event on April 27, 2000 contained detectable concentrations of herbicides in the waterways. 2,4-D concentration peaked at 0.241 ppb at hour two and decreased thereafter. Triclopyr peaked at 0.388 ppb at hour three and then decreased thereafter.

All concentrations measured were well below the North Coast Regional Water Quality Control Board's (Regional Water Board) Water Quality Control Plan for the North Coast Region operational standard of 10 ppb.

Table 4. Concentrations of herbicides in tank samples.

Date	Time	Sample type	Site	2,4-D	Triclopyr	Atrazine
3/23/00	07:55	Tank	H	-- ^a	--	4.47%
4/22/00	09:15	Tank	I	1.06%	1.08%	--
4/24/00	11:45	Tank	J	1.46%	1.47%	--
4/24/00	12:30	Tank	K	--	--	2.50%

a= herbicide not used and hence not analyzed.

Table 5. Concentrations of herbicides in surface water samples taken on the day of aerial application.

Date	Time	Sample type	Site	2,4-D	Triclopyr
04/23/00	08:26	Water	I	ND ^a	ND
04/23/00	08:28	Water	I	ND	ND
04/23/00	08:30	Water	I	ND	ND
04/23/00	08:32	Water	I	ND	ND
04/23/00	08:34	Water	I	ND	ND
04/23/00	09:26	Water	I	0.163 ppb	0.223 ppb
04/23/00	10:26	Water	I	0.491 ppb	1.06 ppb
04/23/00	11:26	Water	I	0.584 ppb	1.02 ppb
04/24/00	11:27	Water	J	ND	ND
04/24/00	11:29	Water	J	ND	ND
04/24/00	11:31	Water	J	ND	ND
04/24/00	11:33	Water	J	ND	ND
04/24/00	11:35	Water	J	ND	ND
04/24/00	12:27	Water	J	ND	ND
04/24/00	13:27	Water	J	ND	ND
04/24/00	14:27	Water	J	ND	ND

a= ND-none detected at the reporting limit for that chemical.

Minimum Reporting Limit: triclopyr and 2,4-D = 0.1 ppb

Table 6. Concentrations of herbicides in runoff surface water samples.

Date	Time	Sample type	Site	2,4-D	Triclopyr	Atrazine
4/16/00	12:40	Water	H	-- ^a		ND ^b
4/16/00	13:40	Water	H	--		ND
4/16/00	14:40	Water	H	--		ND
4/16/00	15:40	Water	H	--		ND
4/16/00	16:40	Water	H	--		ND
4/16/00	17:40	Water	H	--		ND
4/16/00	18:40	Water	H	--		ND
4/16/00	19:40	Water	H	--		ND
04/25/00	10:14	Water	J	0.103 ppb	0.122 ppb	--
04/25/00	07:28	Water	K	--	--	ND
04/25/00	08:28	Water	K	--	--	ND
04/25/00	09:28	Water	K	--	--	ND
04/25/00	10:28	Water	K	--	--	ND
04/25/00	11:28	Water	K	--	--	ND
04/25/00	12:28	Water	K	--	--	ND
04/25/00	13:28	Water	K	--	--	ND
04/25/00	14:28	Water	K	--	--	ND
4/27/00	12:36	Water	M	ND	ND	--
4/27/00	13:36	Water	M	ND	ND	--
4/27/00	14:36	Water	M	ND	ND	--
4/27/00	15:36	Water	M	ND	ND	--
4/27/00	16:36	Water	M	ND	ND	--
4/27/00	17:36	Water	M	ND	ND	--
4/27/00	18:36	Water	M	ND	ND	--
4/27/00	19:36	Water	M	ND	ND	--
4/27/00	13:22	Water	L	ND	ND	--
4/27/00	14:22	Water	L	0.146 ppb	0.195 ppb	--
4/27/00	15:22	Water	L	0.241 ppb	0.362 ppb	--

Date	Time	Sample type	Site	2,4-D	Triclopyr	Atrazine
4/27/00	16:22	Water	L	0.218 ppb	0.388 ppb	--
4/27/00	17:22	Water	L	0.232 ppb	0.383 ppb	--
4/27/00	18:22	Water	L	0.190 ppb	0.319 ppb	--
4/27/00	19:22	Water	L	0.163 ppb	0.293 ppb	--
4/27/00	20:22	Water	L	0.152 ppb	0.285 ppb	--

a= herbicide not used and hence not analyzed.

b= ND-none detected at the reporting limit for that chemical.

Minimum Reporting Limit: atrazine = 0.05 ppb, triclopyr and 2,4-D = 0.1 ppb

Environmental Measurements

Table 7 presents the data for pH, DO, temperature, and EC. Water temperature ranged from 8.5 to 10.7 °C, DO ranged from 9.69 to 11.18 mg/L, and pH values ranged from 6.9 to 7.2. EC ranged from 42.5 to 62.0 µS/cm. The California Regional Water Quality Control Board (RWQCB) (1994), lists the following water quality guidelines as acceptable for the Lower Klamath River hydrologic area (HA): DO above 8.0 mg/L, pH between 6.5 and 8.5, and EC below 200 µS/cm 90% of the time (90% Upper Limit) and below 125 µS/cm 50% of the time (50% Upper Limit). The plans do not provide an acceptable range for temperature, but the Lower Klamath River HA is designated as cold interstate water and its natural receiving water temperature shall not be altered. All water quality measurements taken fall within the RWQCB's acceptable guidelines.

Table 7. Water quality measurement at sampling sites.

Date	Site	Temperature (°C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (µS/cm)
4/16	Bear Creek (H)	10.3	7.2	11.02	46.4
4/23	Hunter Creek (I)	8.5	7.2	11.18	61.8
4/24	Hunter Creek (J)	10.7	6.9	9.69	62.0
4/25	Blue Creek (K)	9.4	7.0	10.85	42.5
4/28	Hunter Creek (L)	9.4	7.0	11.0	58.9
4/28	Hunter Creek tributary (M)	9.5	7.2	10.93	55.8

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References

The California Regional Water Quality Control Board. 1994. Water Quality Control Plan for the North Coast (Basin Plan). Region 1, North Coast Region. Santa Rosa, California.